Fe–Mo alloy coatings as cathodes in chlorate production process

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Abstract

The aim of this study was to gain a better understanding of the feasibility of partial replacement of dichromate, Cr(VI), with phosphate buffer, focusing on the cathode reaction selectivity for hydrogen evolution on mild steel and Fe–Mo cathodes in undivided cell for chlorate production. To evaluate the ability of phosphate and Cr(VI) additions to hinder hypochlorite and chlorate reduction, overall current efficiency (CE) measurements in laboratory cell for chlorate production on stationary electrodes were performed. The concentration of hypochlorite was determined by a conventional potentiometric titration method using 0.01 mol dm^{-3} As$_2$O$_3$ solution as a titrant. The chlorate concentration was determined by excess of 1.0 mol dm^{-3} As$_2$O$_3$ solution and excess of arsenic oxide was titrated with 0.1 mol dm^{-3} KBrO$_3$ solution in a strong acidic solution. Cathodic hypochlorite and chlorate reduction were suppressed efficiently by addition of 3 g dm^{-3} dichromate at both cathodes, except that Fe–Mo cathode exhibited higher catalytic activity for hydrogen evolution reaction (HER). The overvoltage for the HER was around 0.17 V lower on Fe–Mo cathode than on mild steel at the current density of 3 kA m^{-2}. It was found that a dichromate content as low as 0.1 g dm^{-3} is sufficient for complete suppression of cathodic hypochlorite and chlorate reduction onto Fe-Mo catalyst in phosphate buffering system (3 g dm^{-3} Na$_2$HPO$_4$ + NaH$_2$PO$_4$). The overall current efficiency was practically the same as in the case of the presence of 3 g dm^{-3} dichromate buffer (98%). However, for the mild steel cathode, the overall current efficiency for the chlorate production was somewhat lower in the above mentioned mixed phosphate + dichromate buffering system (95%) than in the pure dichromate buffering solution (97.5%).

Keywords: chlorate production, current efficiency, Fe–Mo cathode catalyst, phosphate buffer.

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Sodium chlorate, NaClO$_3$, is mainly used for the production of chlorine dioxide, ClO$_2$, a bleaching agent in the pulp and paper industry. In the electrolytic sodium chlorate production, the main electrode reactions are hydrogen and chlorine formation (reactions (1) and (2)) similar to those in the chlor-alkali process. As chlorate cells are undivided, chlorine undergoes hydrolysis and disproportionates to form hypochlorous acid and hypochlorite (reactions (3) and (4)). Maximal current yield in chlorate production is obtained when the conversion of the hypochlorous species into chlorate occurs only directly by the Foerster reaction of chemical chlorate formation [1] (reaction (5)). The optimum rate of reaction (5) takes place at pH of 6–7 and, accordingly, the electrolyte should be set in that pH range.

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$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \tag{1}$$
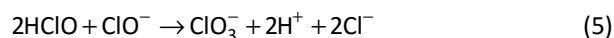
$$2Cl^- \rightarrow Cl_2 + 2e^- \tag{2}$$

$$Cl_2 + H_2O \rightarrow HClO + H^+ + Cl^- \tag{3}$$

$$HClO \rightleftarrows H^+ + ClO^- \tag{4}$$

$$2HClO + ClO^- \rightarrow ClO_3^- + 2H^+ + 2Cl^- \tag{5}$$

The second and almost unavoidable path represents another Foerster reaction of further anodic oxidation of hypochlorite to the final state:

$$6ClO^- + 2H_2O \rightarrow 2ClO_3^- + 4H^+ + 4Cl^- + O_2 + 6e^- \tag{6}$$
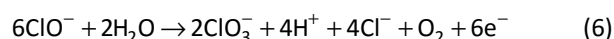
This is also known as the reaction of electrochemical chlorate formation [2] and represents the corresponding current losses.

In addition to the hydrogen evolution reaction, two other reduction processes could theoretically take place at the cathode and would lead to further current losses:

$$ClO^- + H_2O + 2e^- \rightarrow Cl^- + 2OH^- \tag{7}$$

$$ClO_3^- + 3H_2O + 6e^- \rightarrow Cl^- + 6OH^- \qquad (8)$$
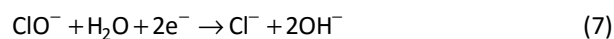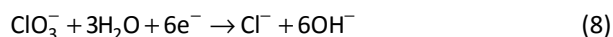
DSA$^®$ anode or platinum–iridium-coated titanium are currently used as anodes and their high electro-catalytic activity for chloride oxidation ensures that, apart from the Foerster reaction of electrochemical chlorate formation (Eq. (6)), the current losses due to anodic water oxidation can be completely neglected because of the much more positive potential for this reaction.

Cathodic current losses have so far been efficiently suppressed by addition of small amounts of dichromate (about 2–4 g dm^{-3}), after Müller [3], which also acts as a pH buffer providing and maintaining the optimal pH range for the chemical conversion of available chlorine to chlorate, and alters the potential of the DSA$^®$ anode [4]. In addition, the chromate may have a retarding effect on the corrosion of steel cathodes [5]. During cathodic polarization Cr(VI) becomes reduced to Cr(III) and forms a thin film of chromium(III) hydroxide on the cathode [6]. This film hinders the unwanted side reactions (7) and (8), while hydrogen evolution can still take place, though with changed kinetics [7]. The thickness and growth rate of the chromium(III) hydroxide film depends on factors such as: the cathode material, the electrode potential and the chromate concentration [8]. Although low chromate concentration as 0.1 g dm^{-3} Cr$_2$O$_7^{2-}$ has been shown to efficiently hinder reduction of Fe(CN)$_6^{3-}$ on smooth platinum electrode [9], in the chlorate production the concentration of dichromate should be much higher (3–8 g dm^{-3}) [10]. However, a higher overpotential for hydrogen evolution reaction (HER) was obtained for iron and platinum in the presence of Cr(VI) [11]. The overpotential of the HER on mild steel is quite high (about 500 mV) in the presence of dichromate, which directly affects the specific power consumption. It is estimated that power consumption can be lowered by 10–15%, if the overpotential of the HER is reduced by 100 mV [12]. The presence of dichromate in addition to the chlorate crystals appears to be undesirable in the chlorine dioxide generation process, since both salts (chlorate and dichromate) are highly soluble and it is difficult to separate them by crystallization. Dichromate in the chlorate liquor must be less than 0.5 wt.% during sodium chlorate crystallization [13], otherwise the crystal product will exhibit a characteristic yellowish color.

Many attempts have been made so far to replace, or at least to reduce, the dichromate content in the electrolyte of chlorate cells. The aim of the present paper is to present some achievements in this respect.

EXPERIMENTAL PROCEDURE AND APPARATUS

Determination of the hypochlorite and chlorate concentrations using an improved potentiometric titration method

In our experiments the following procedure was found to give sufficiently accurate results: the sum of the concentrations of available chlorine (hypochlorite, hypochlorous acid, and dissolved molecular chlorine) and the concentration of chlorate were determined using an improved potentiometric titration method, based on a procedure given by Norkus and Prokopchik [14].

Solution for determination of the hypochlorite concentration

The concentration of hypochlorite was determined by a conventional potentiometric titration method using 0.01 mol dm^{-3} As$_2$O$_3$ solution as a titrant. Reaction between As$_2$O$_3$ and active chlorine can be presented by the following equation:

$$As_2O_3 + 2ClO^- \rightarrow As_2O_5 + 2Cl^- \qquad (9)$$
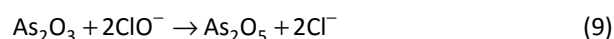
Solution for determination of the chlorate concentration

The chlorate concentration was determined by excess of 1.0 mol dm^{-3} As$_2$O$_3$ solution and excess of arsenic oxide was titrated with 0.1 mol dm^{-3} KBrO$_3$ solution in a strong acidic solution.

For potentiometric determination of chlorate it is necessary to prepare the following solutions: 1.0 mol dm^{-3} As$_2$O$_3$; 0.1 mol dm^{-3} KBrO$_3$; 37 wt.% HCl; 30 g dm^{-3} NaBr.

The reactions between arsenic oxide and chlorate and bromate are given as:

$$3As_2O_3 + 2ClO_3^- \rightarrow 3As_2O_5 + 2Cl^- \qquad (10)$$

$$3As_2O_3 + 2BrO_3^- \rightarrow 3As_2O_5 + 2Br^- \qquad (11)$$
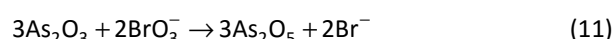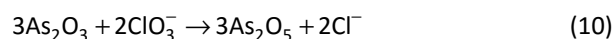
The unknown concentration of chlorate can be calculated by the following equation:

$$c(ClO_3^-) = \frac{c(As_2O_3)V(As_2O_3)}{1.5} - c(BrO_3^-)V(BrO_3^-) \qquad (12)$$

where: $c(As_2O_3)$ – the concentration of arsenic oxide solution added in excess, after reaching the hypochlorite endpoint (1.0 mol dm^{-3}); $V(As_2O_3)$ – the volume of arsenic oxide solution added in excess, after reaching the hypochlorite endpoint (2 cm^3); $c(BrO_3^-)$ – the concentration of bromate solution for potentiometric titration of arsenic oxide excess (0.1 mol dm^{-3}); $V(BrO_3^-)$ – the volume of bromate solution for potentiometric titration of arsenic oxide excess.

Analytical

The sample of 1 cm^3 was taken from the electrolyte solution at suitable intervals during the electrolysis. The analytical procedure was carried on at room temperature. After addition of some saturated solution of sodium bicarbonate to the sample, available chlorine was titrated potentiometrically with a solution of 0.01 mol dm^{-3} As$_2$O$_3$ in a 100 cm^3 beaker containing a platinum ring electrode and a calomel reference electrode (SCE). Before each run the platinum electrode was shortly immersed in a mixture of concentrated sulfuric and nitric acids and thoroughly washed with distilled water. After reaching the hypochlorite endpoint excess arsenic oxide solution was added (2 cm^3 of 1.0 mol dm^{-3} As$_2$O$_3$), some sodium bromide solution (about 30 mg, or 1 cm^3 of 30 g dm^{-3} NaBr solution) and a volume of chemically pure concentrated hydrochloric acid approximately equal to the solution volume already present in the beaker. The solution which contained now at least 20 wt.% HCl was then allowed to stand for 5–7 min. After that time the excess As$_2$O$_3$ was titrated potentiometrically with 0.1 mol dm^{-3} KBrO$_3$ solution. The relative potential change was followed using a potentiometer. The shape of the potentiometric titration curves is illustrated in Fig. 1. The accuracy of the chlorate concentration values determined by the described method was better than ±2%, for chlorate concentrations not smaller than 0.001 mol dm^{-3}.
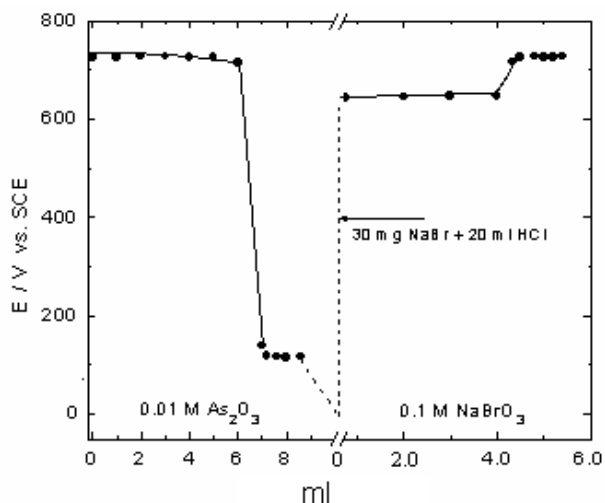

Fig.1. Potentiometric titration curves for hypochlorite and chlorate with As$_2$O$_3$.

Apparatus for simulation of chlorate production process

The experimental set-up is shown schematically in Fig. 2. The temperature throughout the whole volume was maintained constant by circulating the thermostatic liquid through a glass cooling coil situated in back-mix flow reactor. The desired pH value within the

entire volume was controlled by adding 37 wt.% hydrochloric acid from an automatic titrator. The electrical set-up consisted of a constant d.c. supply, a multirange Amper–Volt-meter with a high internal impedance. Two types of cathodes (mild steel and Fe–Mo alloy coated mild steel) and activated titanium DSA® anode were used in the experiments. The electrodes had a rectangular shape (4 cm×5 cm) with a projected surface area of 20 cm^2, and were placed face to face in a vertical position with an interelectrode gap of 3 mm to form the main part of the cell. Intensive electrolyte flow within the cell was provided by the gas-lifting effect of cathodically generated hydrogen. The high recirculation rate led to a negligible difference in the available chlorine and chlorate contents in the cell and in the total volume of electrolyte.
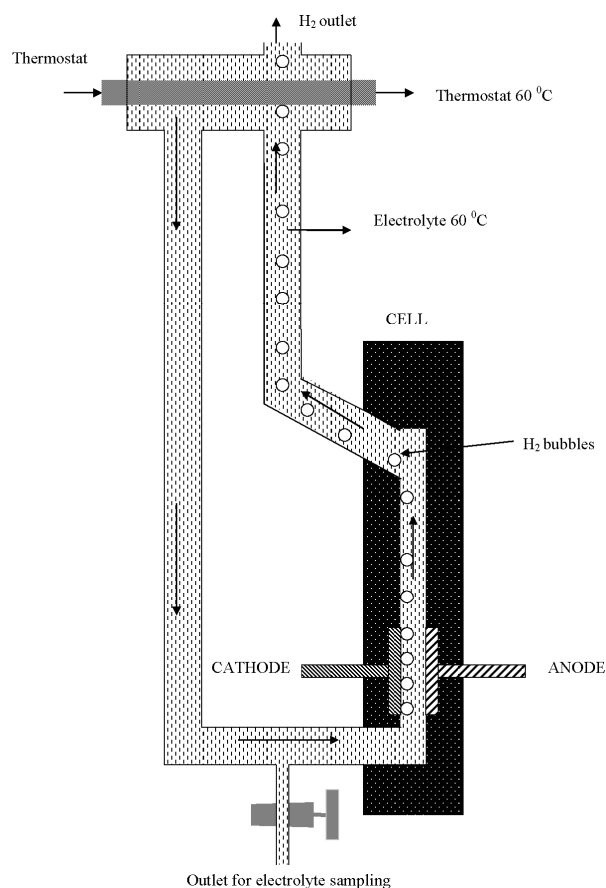

Fig. 2. The experimental set-up for continuous flow chlorate cell process.

Working conditions

Starting solutions: A) 300 g dm^{-3} NaCl + 3 g dm^{-3} K$_2$Cr$_2$O$_7$; B) 300 g dm^{-3} NaCl + 3 g dm^{-3} (NaH$_2$PO$_4$ + Na$_2$HPO$_4$) + 0.1 g dm^{-3} K$_2$Cr$_2$O$_7$; temperature 60±2 °C; pH 6.3–6.6; total volume of electrolyte, 0.3 dm^3; current density, 2.5 kA m^{-2} (active surface area = 20 cm^2, and total current I = 5 A); anode: activated titanium

anode (35 mol.% RuO_2 + 65 mol.% TiO_2 with 10 g m^{-2} RuO_2, home-made); cathode: 1) mild steel; 2) mild steel coated with Fe–Mo alloy catalyst.

Preparation of Fe–Mo alloy coatings onto mild steel

The mild steel substrates were first degreased in NaOH-saturated ethanol solution for 5 min. and then etched by immersion in 25 wt.% HCl for 2 min. After this procedure sample was washed with distilled water, dried and weighted and then immersed in the solution for Fe–Mo alloy deposition. After deposition samples were washed, dried and weighted again to determine the mass of the alloy. All solutions were made using distilled water and analytical grade chemicals.

Fe–Mo alloys were deposited at a constant current density of –100 mA cm^{-2} from the plating bath with the following composition: 9 g dm^{-3} $FeCl_3$, 40 g dm^{-3} Na_2MoO_4, 75 g dm^{-3} $NaHCO_3$ and 45 g dm^{-3} $Na_4P_2O_7$ at 60 °C. A Pt mesh, placed parallel to the cathode, was used as a counter electrode during the alloy deposition and electrolyte was moderately stirred with the magnetic stirrer. Fe–Mo coating thickness was approximately 20 μm consisting of 47 mass% Mo and 53 mass% Fe (energy dispersive X-ray spectroscopy (EDS) analysis was used to determine alloy composition). Certain amount of oxygen was also detected, but the content was calculated neglecting detected amount of oxygen.

Polarization curve measurements

Polarization curve measurements for mild steel and Fe–Mo alloy coatings were performed with the potentiostat Reference 600 and software DC 105 in a standard electrochemical cell. Potential was changed with a rate of 1 mV s^{-1} and was corrected for the IR_Ω drop by current interrupt technique. Silver/silver chloride electrode (Ag/AgCl) was used as a reference electrode, while Pt mesh was used as a counter electrode. Before recording polarization diagrams electrodes were exposed to hydrogen evolution in the same solution at $j =$ = –0.1 A cm^{-2} for 10 min.

RESULTS AND DISCUSSION

Polarization measurements in the absence and presence of phosphate and dichromate

Polarization diagrams for mild steel and Fe–Mo alloy coatings, recorded in the solution containing 300 g dm^{-3} NaCl + 150 g dm^{-3} NaClO$_3$ at 60 °C are presented in Fig. 3a, while those recorded in the phosphate buffering system (solution B) with addition of different amounts of $K_2Cr_2O_7$ are shown in Fig. 3b. As can be seen the addition of dichromate influences polarization curves for both electrodes, changing (increasing) their slopes at lower current densities. More pronounced influence of the addition of phosphate buffer and
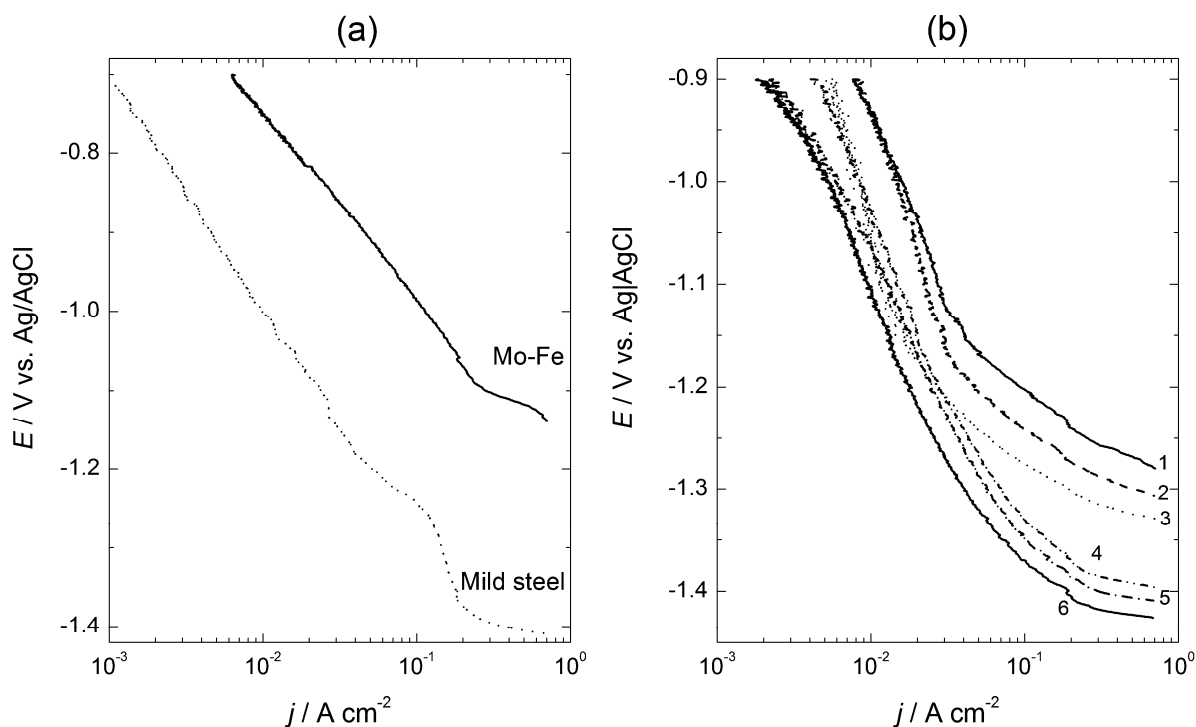
Fig. 3. a) Polarization diagrams for mild steel and Fe–Mo alloy coatings recorded in the solution containing 300 g dm^{-3} NaCl + 150 g dm^{-3} NaClO$_3$ at 60 °C. b) Polarization diagrams for mild steel (4–6) and Fe–Mo (1–3) alloy coatings recorded in the solution containing 300 g dm^{-3} NaCl + 150 g dm^{-3} NaClO$_3$ at 60 °C in the phosphate buffering system (3 g dm^{-3} (NaH$_2$PO$_4$ + Na$_2$HPO$_4$)) with addition of dichromate: 1 and 4–0.05 g dm^{-3} K$_2$Cr$_2$O$_7$; 2 and 5 – 0.10 g dm^{-3} K$_2$Cr$_2$O$_7$; 3 and 6 – 1.00 g dm^{-3} K$_2$Cr$_2$O$_7$.

dichromate on the potential has been detected for the Fe–Mo cathode (increasing overvoltage for about 0.1 V). It is interesting to note that with increasing amount of dichromate catalytic activity of both electrodes decreases, indicating that the addition of very small amount of dichromate (0.05 g dm^{-3}) would be satisfactory for preventing hypochlorite and chlorate reduction on the cathode surface in the investigated system.

Chlorate cell process with dichromate buffer (commercial electrolyte)

The values of the hypochlorite and chlorate concentrations during the electrolysis of solution A with the mild steel and with Fe–Mo cathodes, obtained in the apparatus schematically presented in Fig. 2, are given in Tables 1 and 2, respectively.

As can be seen from Tables 1 and 2, significant difference is recorded for the cell voltage, being for about 0.15 V lower for the Fe–Mo cathode, while other parameters are very similar.

The corresponding faradaic yields for chlorate cell process are presented in Fig. 4a. Slightly better faradaic

yields have been achieved with Fe–Mo cathode. The results presented in Tables 1 and 2 (cell voltage) and in Fig. 4a (faradaic yield, η_j) clearly indicate higher catalytic activity for the hydrogen evolution reaction on the Fe–Mo alloy coating (lower amount of the ClO^- could be reduced at the cathode surface) in comparison with that on mild steel cathode in the presence of dichromate buffer.

The voltage *vs*. current characteristics for the cell with the mild steel and the Fe–Mo alloy coating as cathodes are presented in Fig. 4b. As can be seen the difference between the cell voltage with mild steel and Fe–Mo alloy coating becomes more pronounced at higher current densities, reaching the value of about 0.17 V at the current density of 3 kA m^{-2}.

Chlorate cell process with phosphate buffer

As already mentioned cathodic current losses during chlorate production have so far been efficiently suppressed by small addition of dichromate (3–5 g dm^{-3}) [2]. In fact, dichromate provides several benefits for the electrochemical process of chlorate production: a)

Table 1. Hypochlorite and chlorate concentrations, pH, temperature and cell voltage during chlorate cell process: starting solution 300 g dm^{-3} NaCl + 3 g dm^{-3} $K_2Cr_2O_7$; I = 5 A; mild steel cathode

τ / h	pH	t / °C	Cell voltage, V	$c(ClO^-)$ / mol dm^{-3}	$c(ClO_3^-)$ / mol dm^{-3}
0.0	6.41	61.0	3.17	–	–
1.0	6.48	61.5	3.15	0.070	0.098
1.5	6.46	61.0	3.16	0.06	0.148
2.0	6.58	61.3	3.16	0.06	0.200
3.0	6.50	62.0	3.14	0.06	0.299
3.5	6.59	62.0	3.14	0.06	0.350
4.0	6.6	61.8	3.15	0.06	0.400
5.0	6.59	61.4	3.16	0.06	0.491
6.0	6.48	60.8	3.15	0.06	0.600
6.5	6.6	61.0	3.15	0.06	0.650
7.0	6.52	61.2	3.16	0.06	0.700
8.0	6.47	61.4	3.16	0.065	0.798

Table 2. Hypochlorite and chlorate concentrations, pH, temperature and cell voltage during chlorate cell process: starting solution 300 g dm^{-3} NaCl + 3 g dm^{-3} $K_2Cr_2O_7$; I = 5 A; Fe–Mo coating cathode

τ / h	pH	t / °C	Cell voltage, V	$c(ClO^-)$ / mol dm^{-3}	$c(ClO_3^-)$ / mol dm^{-3}
0.0	6.42	61.0	3.01	–	–
0.25	6.48	61.5	3.02	0.055	0.024
0.67	6.18	61.0	3.02	0.06	0.067
1.0	6.42	61.3	3.01	0.06	0.100
2.0	6.36	62.0	3.01	0.06	0.202
3.0	6.37	62.0	3.02	0.06	0.304
4.0	6.58	61.8	3.01	0.06	0.405
5.3	6.52	61.4	3.02	0.06	0.537
6.0	6.58	60.8	3.01	0.06	0.607
7.0	6.24	61.0	3.01	0.055	0.709
8.0	6.39	61.2	3.02	0.06	0.810

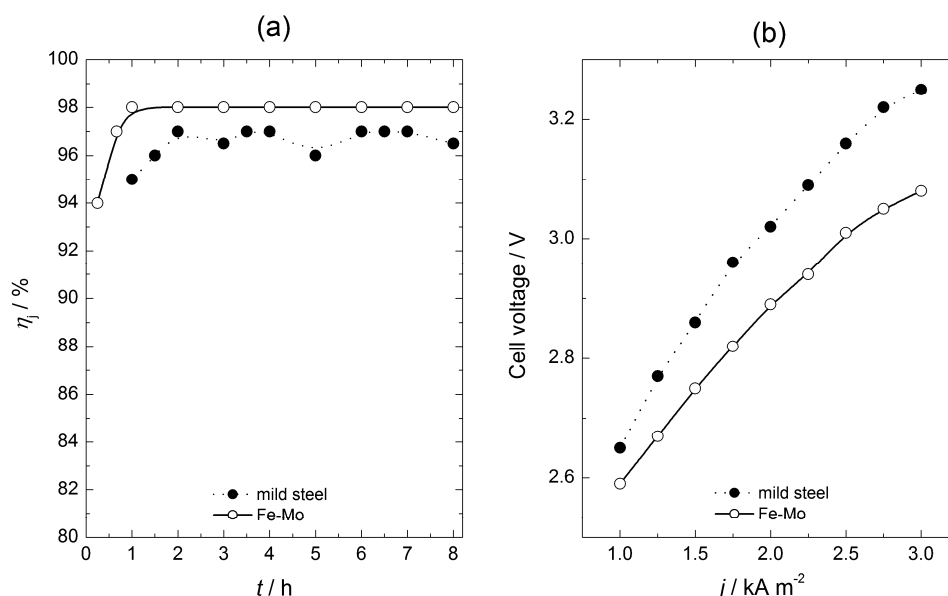*Fig. 4. a) Faradaic yields for chlorate cell process with dichromate buffer (3 g dm^{-3} K$_2$Cr$_2$O$_7$) for different cathode materials. b) Cell voltage vs. current density for chlorate cell process with dichromate buffer (3 g dm^{-3} K$_2$Cr$_2$O$_7$) for different cathode materials.*

completely suppresses the hypochlorite reduction at the cathode; b) provides and maintains the optimal pH region for the chemical conversion of available hypochlorite to chlorate; c) prevents the corrosion of the steel cathode. However, the presence of dichromate in addition to chlorate crystals appears to be undesirable in the chlorine dioxide generation process, and since both salts (chlorate and chromate) are highly soluble it is difficult to separate them by crystallization. Thus, many attempts have been made to replace, or at least to reduce, the dichromate content in the electrolyte of chlorate cells. The aim of the present investigations is to present the experimental results for chlorate production for two types of cathode materials for the following buffering system: a proper mixture of primary and secondary phosphate buffer (3 g dm^{-3} in total) + 0.1 g dm^{-3} dichromate. For above maintained buffering system dichromate is in an almost negligible amount, for 12–15 times lower than the content in normal industrial practice.

The values of the hypochlorite and chlorate concentrations during the electrolysis of solution B with the mild steel and the Fe–Mo alloy coating cathodes are presented in Tables 3 and 4, respectively.

Considering the results presented in Tables 3 and 4 the same conclusion, as in the case of the commercial electrolyte (Tables 1 and 2), can be made. The obtained results can be explained by different competitive phosphate and dichromate ions adsorption onto mild steel and Fe–Mo electrodes.

Figure 5 shows the experimentally achieved dependence of the faradaic yields of chlorate production during the electrolysis for both cathodes in phosphate buffering system. It was found in the present investigation that a dichromate content as low as 0.1 g dm^{-3} is adequate for complete protection against cathodic hypochlorite reduction onto Fe–Mo catalyst and faradaic yields are practically the same as in the case of the presence of 3 g dm^{-3} dichromate buffer. However, for the mild steel cathode, the faradic yields for the chlor-

Table 3. Hypochlorite and chlorate concentrations, pH, temperature and cell voltage during chlorate cell process: starting solution 300 g dm^{-3} NaCl + 3 g dm^{-3} (Na$_2$HPO$_4$ + NaH$_2$PO$_4$) + 0.1 g dm^{-3} K$_2$Cr$_2$O$_7$; I = 5 A; mild steel cathode

τ / h	pH	t / °C	Cell voltage, V	c(ClO$^-$) / mol dm^{-3}	c(ClO$_3^-$) / mol dm^{-3}
0.0	6.42	60.0	3.17	–	–
1.0	6.35	61.2	3.09	0.075	0.088
2.0	6.46	61.5	3.09	0.065	0.184
3.0	6.52	61.4	3.11	0.07	0.282
4.0	6.43	60.8	3.12	0.07	0.380
5.0	6.57	61.0	3.12	0.06	0.481
6.0	6.60	61.2	3.13	0.075	0.589
7.0	6.53	61.1	3.12	0.07	0.687
8.0	6.48	61.4	3.13	0.07	0.777

Table 4. Hypochlorite and chlorate concentrations, pH, temperature and cell voltage during chlorate cell process: starting solution 300 g dm^{-3} NaCl + 3 g dm^{-3} (Na$_2$HPO$_4$ + NaH$_2$PO$_4$) + 0.1 g dm^{-3} K$_2$Cr$_2$O$_7$; I = 5 A; Fe–Mo coating cathode

τ / h	pH	t / °C	Cell voltage, V	$c(ClO^-)$ / mol dm^{-3}	$c(ClO_3^-)$ / mol dm^{-3}
0.0	6.40	60.0	3.00	–	–
1.0	6.44	61.3	2.97	0.060	0.100
2.0	6.70	61.5	2.97	0.065	0.202
3.0	6.77	62.0	2.97	0.060	0.304
4.0	6.45	61.4	2.96	0.060	0.405
5.0	6.65	61.5	2.96	0.060	0.506
6.0	6.60	61.0	2.97	0.060	0.607
7.0	6.62	61.2	2.97	0.060	0.672
8.0	6.52	61.1	2.97	0.055	0.810

ate production are somewhat lower in the phosphate buffering system (3 g dm^{-3} (NaH$_2$PO$_4$ + Na$_2$HPO$_4$)) with addition of 0.1 g dm^{-3} K$_2$Cr$_2$O$_7$ than in the dichromate buffering solution (commercial electrolyte, Fig. 4a).

It is interesting to note that the cell voltages are also somewhat lower (40–50 mV) in the phosphate buffering electrolyte with both types of cathode materials (Fig. 6), which could be of practical importance for industrial chlorate practice. The lower cell voltage could be explained by different influence of adsorbed phosphate or dichromate ions on the kinetics of the hydrogen evolution reaction at the investigated cathode materials. Some of the results presented in this paper are included in the recent international patent [15].
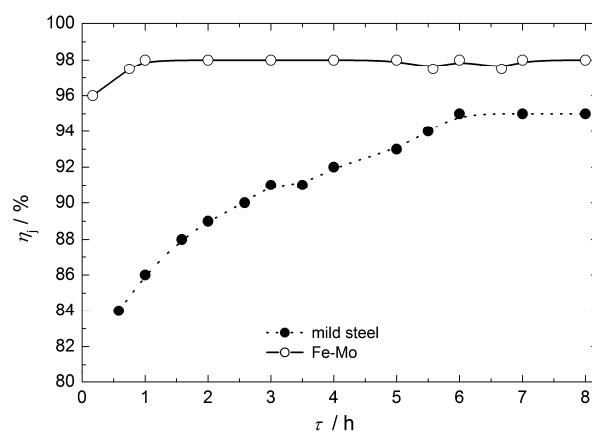

Fig. 5. The variation of faradaic yields in the chlorate cell process during electrolysis in phosphate buffering electrolyte (3 g dm^{-3} (Na$_2$HPO$_4$ + NaH$_2$PO$_4$)) with addition of 0.1 g dm^{-3} K$_2$Cr$_2$O$_7$ for mild steel and Fe–Mo cathode materials.
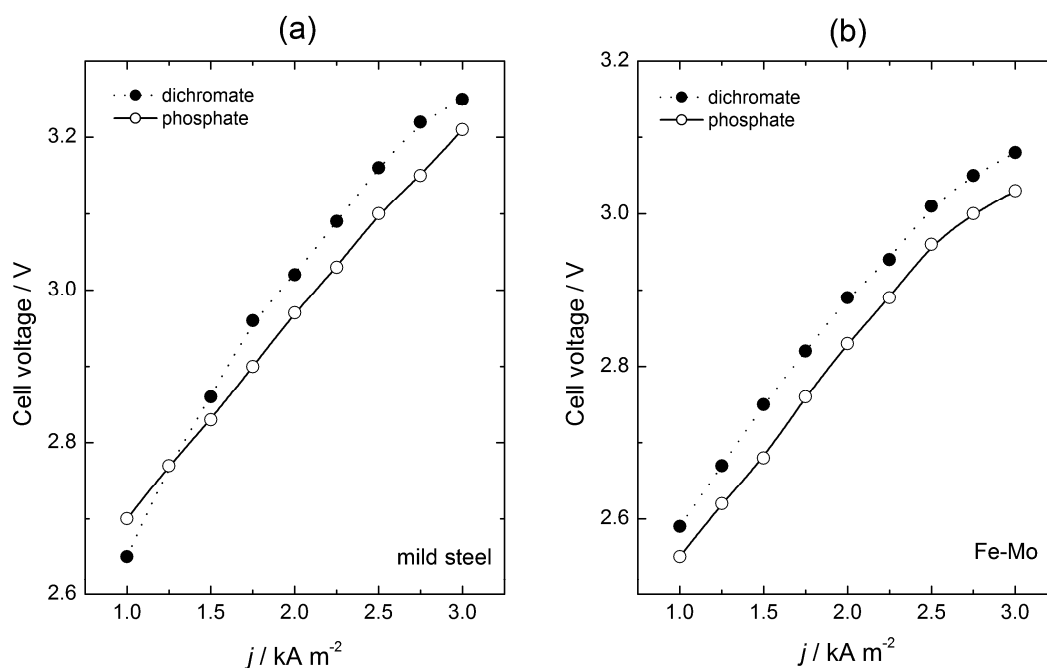

Fig. 6. Cell voltage vs. current density for chlorate cell process with dichromate (3 g dm^{-3} K$_2$Cr$_2$O$_7$) and phosphate buffers (3 g dm^{-3} (Na$_2$HPO$_4$ + NaH$_2$PO$_4$) + 0.1 g dm^{-3} K$_2$Cr$_2$O$_7$) for different cathode materials.

CONCLUSIONS

– Current efficiency experiments in pure dichromate buffering solution for chlorate production showed that high overall current efficiencies have been achieved at both mild steel and Fe-Mo cathodes.

– When starting the electrolysis, the current efficiency was initially low, but increased with time of electrolysis with the both cathode materials.

– Fe–Mo cathode exhibited the higher catalytic activity for the HER than the mild steel cathode**.** The difference between the cell voltage with mild steel and Fe––Mo alloy coating becomes more pronounced at higher current densities, reaching the value of about 0.17 V at the current density of 3 kA m^{-2}.

– It was found that a dichromate content as low as 0.1 g dm^{-3} is adequate for complete suppression of cathodic hypochlorite and chlorate reduction onto Fe––Mo catalyst in phosphate buffering system (3 g dm^{-3} Na$_2$HPO$_4$ + NaH$_2$PO$_4$). The overall current efficiency was practically the same as in the case of the presence of 3 g dm^{-3} dichromate buffer (98%).

– The overall current efficiency for the chlorate production with mild steel cathode was somewhat lower in the mixed phosphate + dichromate buffering system (95%) than in the pure dichromate buffering solution (97.5%).

– From the results obtained with stationary polarization measurements and the results of testing the process of chlorate production in the test cell (simulation of the industrial process) it could be concluded that the application of phosphate and dichromate buffering system with Fe–Mo alloy as a cathode might be promising technology for chlorate production.

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IZVOD

PREVLAKE OD Fe–Mo LEGURA KAO KATODE U PROIZVODNJI HLORATA

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(Naučni rad)

Cilj ovih istraživanja je bio da se ispita mogućnost delimične zamene dihromata sa fosfatnim puferom u proizvodnji hlorata, razmatranjem pre svega njihovog uticaja na selektivne osobine mekog čelika i Fe–Mo katoda za izdvajanje vodonika. Da bi se ispitala sposobnost fosfata i dihromata u sprečavanju redukcije hipohlorita i hlorata kao sporednih reakcija, odredjivano je ukupno iskorišćenje struje u laboratorisjkoj ćeliji za proizvodnju hlorata sa stacionarnim elektrodama. Koncentracija hipohlorita je odredjivana standardnom potenciometrijskom titracijom korišćenjem rastvora 0,01 mol dm^{-3} As$_2$O$_3$, kao titranta. Koncentracija hlorata je odredjivana pri višku 1,0 mol dm^{-3} As$_2$O$_3$ rastvora, a neizreagovana koncentracija oksida arsena je titrisana sa 0,1 mol dm^{-3} KBrO$_3$ rastvorom u koncentrovanom kiselom rastvoru. Pokazano je da se katodna redukcija hipohlorita i hlorata može uspešno sprečiti dodatkom 3 g dm^{-3} dihromata na navedenim katodnim materijalima, s tim što je Fe–Mo katoda pokazala bolju katalitičku aktivnost za reakciju izdvajanja vodonika. Prenapetost izdvajanja vodnika je bila oko 0.17 V manja na Fe–Mo katodi nego na mekom čeliku, pri gustini struje od 3 kA m^{-2}. Ispitivanja su pokazala da je veoma niska koncentracija dihromata od svega 0,1 g dm^{-3} dovoljna za potpuno suzbijanje nepoželjnih katodni reakcija redukcije hipohlorita i hlorata na Fe–Mo katalizatoru u rastvoru sa fosfatnim puferom (3 g dm^{-3} Na$_2$HPO$_4$ + NaH$_2$PO$_4$). Postignuto je praktično isto iskorišćenje struje kao i u prisustvu 3 g dm^{-3} dihromata kao pufera (98%). Medjutim, iskorišćnje struje korišćenjem mekog čelika kao katodnog materijala je niže u prisustvu pomenutog mešovitog fosfatno-dihromatnog pufera (95%) nego u rastvoru sa dihromatnim puferom (97,5%).